WETTING BEHAVIOR AND CURING KINETICS OF CARBON
NANOFIBERS MODIFIED EPOXY RESINS

By

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Nanoparticles can not only influence many properties of epoxy resins but also affect the wetting behaviors and curing processes of the resulting resins as matrices in using fiber reinforced composites. In this research work, wetting characteristics and curing kinetics of epoxy resins modified by as-received graphitic nanofibers (as-GNFs), oxidized GNFs (ox-GNFs), and a type of reactive GNFs (re-GNFs). The dynamic wetting behavior, surface tension, and viscosity of the modified epoxy matrices were characterized. The experimental results showed that the re-GNFs contributed to improved wetting behaviors for epoxy resins. Furthermore, the re-GNFs modified epoxy also showed reduced viscosity, which was different from increased viscosity in the traditional polymer nanocomposites. The curing processes of the commercial epoxy resin (EPON 828) and the re-GNFs modified epoxy samples were evaluated using differential scanning calorimetry (DSC) under the linear heating
regimes. The activation energy of the two systems was determined based on model-free method. The results indicated that the addition of the re-GNFs offered a catalytic action for cure reaction of epoxy resin at high temperature range so that the larger extent of cure was obtained over pure epoxy. The improved wetting characteristics and faster curing behaviors of the re-GNFs modified epoxy system will be significant for enabling energy efficient infusion processing for manufacturing high quality and high performance structural composite applications.
DEDICATION

Dedicated to my daughter Eunice with love and happiness
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1.1 Fiber/matrix interfacial problems in FRP composites

Because of their superior strength-to-weight ratio, fatigue and fracture resistance, and damping characteristics, advanced fiber-reinforced polymer composites are increasingly needed applied in the aerospace industry as primary structures. These industries require FRP composites exhibit further enhanced reliability and durability. However, in applications manufactured composite structures cannot always reach expectations derived from the properties of the fiber reinforcements and polymer matrices separately. It has been found that the stress-transfer ability of the fiber/matrix interface and, in turn, the mechanical properties of the composites are greatly affected by the level of the interfacial integrity between fiber and matrix [1, 2]. In many cases catastrophic failure occurs in the interface region due to chemical reaction or plastification with water penetrating the fiber/matrix interface. For instance, the tensile strength of the FRP composites are strongly dependent on how well the stress can be transferred from the broken fibers to the surviving fibers through shear stress in the resin and the interfacial areas. In service the weak and unstable interfacial bonding in FRP components lead to the catastrophic failure of the parts because the interfacial debonding can arrest the stress transfer from the matrix to the fiber. A better interfacial bond will impart to a composite better properties such as interlaminar shear strength, delamination resistance, fatigue, and corrosion resistance. Therefore, the fiber/matrix interface plays a leading role in binding and transferring the forces to the fiber, thus determining the mechanical properties of the resulting composites. On the
other hand, durability and reliability of a composite structure also depends on the fiber/matrix interface adhesion to a high degree. Particularly, strength, toughness, fatigue resistance, and the life expectancy of the structural composite are very sensitive to the stability and bonding strength of the fiber/matrix interfaces. The debonding between fiber and matrix will invariably lead to low strength of the final composite products, and the environmental agents, such as water, can migrate to the fiber/matrix interfaces, destroy the initial bonding, and cause degradation of strength properties. In most practical polymer composites a good interfacial bond is hence regarded as being absolutely vital because interfacial strength and stability between fiber and matrix exert significant control over the wide range of properties of fiber-reinforced polymer composites. The interfacial adhesion between the fiber and the matrix has been considered the ‘heart of the composite’ and has been the focus of significant research. So it has become more important to promote the interaction between the reinforcing fibers and the matrix materials.

In the 1970’s, Zisman [3] summarized the condition necessary for good adhesion in FRP composites and pointed out the importance of complete wetting of the fibers by the liquid matrix resin. He also concluded that the properties of FRP composites were dominated by the nonidealities of the interface such as the presence of voids, which were stress concentrators and potential crack initiators. These existing defects probably arise from incomplete resin wetting and penetration into fiber tows and poor adhesion as a result of high interfacial stresses in the fiber/matrix interfacial property mismatch. Today, although the developed processing techniques could minimize the
existing defects such as voids and occlusions, property mismatch between fiber reinforcements and polymer matrices can not be overcome by the processing techniques. The greater property mismatch will result in larger internal stresses at higher temperatures and ultimately fiber/matrix failure of structural parts.

To tackle the aforementioned problems, much research has been devoted to the development of specific fiber surface treatments of FRP composites for improvement of the interfacial adhesion because fiber/matrix interfacial adhesion is strongly dependent on the thermodynamic and the chemical states of the fiber surface. Therefore, there have been many research and technologies focusing on the modification of the surface structure of the fiber. The primary function of the fiber surface treatment is to improve the fiber surface wettability with the matrix, and then to create a strong bonding at the fiber/matrix interface through introducing the active sites on the fiber surface to enhance reactivity of the structure. Interfacial adhesion properties are typically improved by enhancing the chemical interaction at the interface or by increasing the interfacial area, providing a larger area over which to transfer load. Surface area, surface energy, and the acid–base characteristics change with the nature of the fiber surfaces and these can be changed by the surface treatments [2].

In the past decades, surface treatment techniques for fiber reinforcements had been developed to realize good bonding interfacial strength between fiber reinforcements and polymer matrices. The principal fiber reinforcements in commercial use for FRP composites are various types of glass and carbon fibers. The non-active chemical
structure and resulting lack of reactive groups on these fiber reinforcement surfaces cause low surface energy, and thus lead to difficulty in obtaining good wetting and bonding at the fiber/matrix interface, and hence produce poor interlaminar shear strength as well as poor strength and stiffness of the FRP composites. To achieve sufficient wetting, thereby realizing strong bonding at the fiber/matrix interface, this low surface energy on the fiber surfaces requires that the matrix material be of an even lower energy because good wetting and strong interfacial bonding are essential for effective stress transfer from the matrix to the fiber.

Glass fiber-reinforced polymer composites have been used extensively for the past decades, partly owing to the development and use of silane coupling agents. The function of a coupling agent is to promote fiber/matrix adhesion and also to serve as a protective coating for glass fiber surfaces when used in sufficient quantity because a coupling agent can interact chemically or physically with both the fiber surface and the polymer matrix. The interfacial bonding created by silane agents may allow a better load stress transfer between fibers and matrix and in turn improves the tensile strength as well as the interlaminar shear strength of the composite. To prevent the fibers from surface abrasion caused by handling and fiber-fiber contacts, sizing agents are generally applied to the fiber surfaces during the fiber manufacturing process. An optimal sizing can be also used to improve the fiber-matrix adhesion. In practical applications the silane agents are also used as a size along with other components for glass fiber surface. For glass fiber-reinforced polymer composites, glass fiber surfaces are treated to enhance the interfacial bonding and preserve it in a service environment,
particularly in the presence of moisture and at moderate temperatures.

Although a coupling agent has been achieved with great advantage in glass fiber systems, this has not been the case in carbon fiber systems. Carbon fiber surfaces are chemically inactive and must be treated to form surface functional groups that promote good chemical bonding with polymer matrices. Although the graphite crystal surfaces of completely bonded carbon atoms are chemically inert, there are still potential active sites located on the incompletely bonded edges and faults in the structure. Reactions associated with carbon fiber surface treatment may take place at those potential active sites and faults in the structure. Fiber surface treatments may also increase the surface area by creating some micropores or pits on the carbon fiber surface. The increase in surface area provides a larger number of contact points for fiber/matrix bonding. Various approaches have been developed to change the fiber surface chemistry and surface topography simultaneously. The carbon fiber surface treatments include dry and wet oxidation methods [4-8], plasma treatment [9, 10], and electrodeposition [11, 12]. The objective of oxidation treatment is to etch the fiber surfaces by removing the weakly bonded carbon debris and other impurities and introduce the polar hydrophilic oxygen-containing groups on the surfaces. So its wettability and bonding ability to the polymer matrix increase. These treatments also permit some control over the extent of specific surface area. Among the non-oxidative treatments of carbon fiber surfaces the highly effective whiskerization, plasma polymerization, and grafting of polymers deposit more active forms of carbon on the fiber surfaces to enhance reactivity of the fiber surfaces.
The improvement in interfacial bonding strength through fiber surface treatments leads to increase in shear strength. It has been confirmed through the fragmentation tests [13, 14] and the fiber pull-out tests [15]. On the other hand, all these beneficial effects of improved strength properties are inevitably accompanied by a loss in the impact strength and fracture toughness of unidirectional laminates or notched tensile strength of angle ply laminates [16, 17]. It has been observed that the debonding at the fiber–matrix interface needs higher energy dissipation for crack propagation and is hence beneficial for attaining higher fracture toughness.

To manufacture structural FRP composites, resin wettability and flowability are critically important for achieving efficient adhesion and thus high performance composites; this is especially true for resin infusion techniques, an important FRP composite manufacturing approach. The properties of the end FRP composite parts are strongly influenced by the infusion and wetting characteristics of matrix resins during the infusion process in manufacturing [1-3]. Typically, a matrix with lower viscosity can offer good flowability, allow better penetration of the liquid matrix resin into the fiber lay-ups during the processing, and reduce the void formation from the gap/entrapment of air along the fiber-matrix interface. Good wetting behavior of polymer matrices can assist better wet-out of matrix to fiber in the fiber lay-ups, effectively reduce dry spots from incomplete wetting in the preform, and finally improve fiber/matrix bonding strength. Therefore, lower viscosity and good wettability of the matrix material are particularly critical for processibility of the matrix material and the manufacturing of high-performance FRP composites.

Theoretically, either increasing the surface energy of the reinforcement through its surface treatments, or decreasing the surface tension of the matrix, can improve wetting and adhesion in the fiber/polymer matrix interface. It is well known that the
properties of an interface are governed largely by the surface characteristics for the two components, such as fiber reinforcement and matrix, which determine the interactions between them. The adhesion properties between a liquid and a solid contact can be evaluated by the thermodynamic interactions, where wetting behavior occurs.

\[ W_s = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} = \gamma_{SL}(\cos \theta - 1) \]

\[ W_w = \gamma_{SV} - \gamma_{SL} = \gamma_{SL}\cos \theta \]

\[ W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = \gamma_{SL}(1 + \cos \theta) \]  

Where, \( W_s, W_w, W_A, \) and \( \theta \) represent the work of spreading, wetting, adhesion, and the equilibrium contact angle, respectively, during the interactions of the liquid-solid contact.

From these equations, we can conclude that the dissipated work from the liquid-solid interactions increases with the decrease of the equilibrium contact angle \( \theta \). When the equilibrium contact angle is zero, the dissipated work reaches a maximum value. Therefore, the equilibrium contact angle can be used to characterize the wetting behavior of the liquid-solid interactions for the final equilibrium stage of wetting behavior.

Additionally, the equilibrium contact angle can be qualitatively described by Young’s equation, where it can be derived from interaction of a liquid droplet on a solid surface shown in Figure1.1 (a)

\[ \cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \]  

Where, \( \gamma_{SV}, \gamma_{SL}, \) and \( \gamma_{LV} \) are the surface energies of the solid-vapor, solid-liquid, and liquid-vapor. The equilibrium contact angles for 0° and 180° represent the two extreme states of the complete wetting and the complete non-wetting, respectively.
From the above Young’s equation, we can see that a good wetting requires the difference of the solid-vapor surface energy ($\gamma_{SV}$) and the solid-liquid surface energy ($\gamma_{SL}$) approaches the value of the liquid-vapor surface energy ($\gamma_{LV}$). Therefore, wetting is favored when the solid surface energy is high and/or the liquid surface energy is low. These theories resulted in two strategies that have been employed to achieve improved wettability between a solid fiber and a resin matrix. One is to enhance the surface energy of the fiber reinforcements by the fiber surface treatments as summarized in the review; the other is to reduce the surface tension by modifying the characteristics of the polymeric matrix. In other words, there are two common approaches to combat this type of problem, one is to treat the fiber and the other is to operate on the matrix, which is indicated in Figure 1.1 (b). To our knowledge, almost all reported work on improvement in wetting and adhesion at the fiber/matrix interface has been focusing on the study of surface treatments or coating for fiber surface.

To date, there are no reported studies on the improvement of fiber/matrix interface adhesion by fabricating reactive nano-matrix materials. Our proposed approach (see Fig.1.1 (b)) is to fabricate a reactive nano-modified epoxy matrix with low surface tension. Our previous research on carbon nanomaterials has shown that the application of appropriate nano-technology could realize the improvement of fiber/matrix interface adhesion and finally enhance the ultimate performance of fiber reinforced polymer composite materials [18-20].
1.2 State-of-the-art of nanotechnology for enhancing matrix performance

By applying nanotechnology, many researchers have rapidly advanced the state-of-the-art of FRP composites through developing novel reinforcement fibers, strengthening of the interface, and improving matrix properties, as well as developing reliable and lower cost FRP manufacturing technologies.

In the last ten years, nanoscience and technology has offered many versatile possibilities of producing materials with properties beyond that obtained by traditional methods. These improvements in mechanical properties have resulted in major new interest in nanocomposite materials in numerous automotive, aerospace, electronics, biotechnology, and other applications. It is commonly thought that incorporation of nanofillers into polymer matrices and then combining with conventional fiber reinforcements holds great promise of a new generation of multi-functional fiber polymer composite materials. For instance, carbon nanotubes (CNTs) and graphitic carbon nanofibers (GNFs or CNFs), with their exceptionally high aspect ratios and
specific stiffness and strength, make them ideal candidates as nanometric modifiers for matrices in fiber reinforced polymer composites with expanded and enhanced properties. Furthermore, nanotechnology combining CNTs or CNFs with epoxy resins has proven effective to enhance the properties of epoxy matrices through the formation of nanocomposites.

a. CNT-based nanocomposites

Combining CNTs with epoxy resins to form epoxy nanocomposites can significantly improve mechanical properties of polymer matrix. As much as 170% improvement in strength has been reported with only 1 wt% of multi-walled CNTs (MWNTs) with concomitant improvements in fracture toughness and strain to failure [21]. In general, the reported research on CNTs modified resins can be summarized as follows [22-45]:

• Most research was on CNT modified epoxy with concentration levels about 1 – 5 wt%.

• Most research involved oxidized or functionalized CNTs added into epoxy resins; Few studies involved covalent bonding between CNTs and epoxy resins.

• Simple mixtures of treated MWNTs added into epoxy showed limited enhancement in mechanical properties, especially strength and toughness. Dispersion of the functionalized CNTs was still problematic.

• Most results showed enhancements in modulus, but strength showed decreases or limited increases of at most about 10%-15%. However, some researchers obtained over 100% increase in strength vs. the neat epoxy at 1 wt% MWNTs, but in general the results were inconsistent among the different researchers.
Some research reported the effects of nanofillers on the viscosity of nano-modified epoxy resins, but no reported work showed reduced viscosity of the nano-modified epoxy over the pure epoxy.

b. CNF-based nanocomposites

Although the absolute mechanical properties of CNFs are not as high as CNTs, CNFs are low-cost, effective and quality stable carbon nano-fillers, having the potential to be used in a broad class of structural FRP composites. The benefits these nano-fillers can offer are summarized as follows:

1. No need for further purification due to the high purity of commercial products.

Commercial products with extremely high purity graphitic structures are available at very low cost. In particular many CNFs products, such as Pyrograf®, have very high purity levels, i.e. above 98% [46]. Therefore, these commercial CNFs may offer lower price and high quality starting materials.

2. Easy chemical treatments due to the abundant active edges.

The stacked geometry of CNFs (Fig. 1.2) provides an abundance of reactive edges, which are very reactive for chemical modifications and surround each graphene sheet. These highly reactive edges consecrate CNFs with an ease of oxidation and functionalization, thus can dramatically reduce the chemical treatment processing time and energy. Compared to CNTs, CNFs can lead to great potential for application to structural FRP composites where substantial volume needs exist.
Up till now, little research has been done using graphitic nanofibers as reinforcements for FRP composites. The demand for realization of their full potential with a range of exceptional properties is raising new technical challenges. The technical hurdles are believed to originate from their chemical reactivity in molecular structures and high surface area. Due to the weak interfacial bonding to the matrix and their poor solubility in the matrix, their high surface area causes CNFs to have low affinities for other polymers and easily form aggregates in bundle formulation. These drawbacks not only impede their dispersion in most polymer matrices but make them difficult to achieve the strong interfacial bonding and effective load transfer between carbon Nanofibers and polymer matrices. Unless the surface characteristics of the nanofillers are modified, the poor load transfer through the weak interface will lead to an interfacial debonding with consequently poor tensile strengths of the composite. Many efforts have recently been directed at enabling satisfactory dispersibility and strong interfacial interactions of GNFs [47-49]. Surface functionalization is suggested to be an effective way to handle the aforementioned technical barriers, implementing
the anticipated potential for carbon nanofillers as reinforcement materials. For example, Lafdi and Matzuk reported that epoxy composites made with 4 wt% loading of highly oxidized GNF obtained a 35% strength improvement and a 140% modulus improvement.

Recent literature describes surface modification of GNFs by such methods as chemical attachment of functional groups or molecules to improve their chemical reactivity and solubility in the matrix by forming strong interfacial bonding to the matrix. Reported studies showed that the extant chemical interaction between the surface-functionalized GNFs and the resin contributed to a 74% increase in the flexural modulus of GNFs nanocomposite samples [50]. However, in nanocomposites a reduction in strength was often observed as a consequence of this treatment. Besides increases in modulus or stiffness of epoxy resins, it is also desired to enhance strength and toughness for the nano-modified epoxy resins, which has in fact been realized in a nano-epoxy matrix by Lukehart and Zhong [51-53].

The previous studies showed that the simply functionalized nano-fibers, GNF-ODA, could not react with epoxy though GNF-ODA nano-fibers have amino group as the curing agent. However, after they were cut short using a high power sonication at the dispersant of an epoxy diluent (with epoxide group), such as butyl glycidyl ether (BGE), and then reacted with the residual diluent molecules, a kind of oligomeric structure with nano-fibers and highly reactive group, -H*, the so called reactive nano-fibers (re-GNFs), could be obtained. In the structure of re-GNFs, the –OH* could open epoxide ring of epoxy molecules as an amino curing agent reacting
with epoxy to form crosslinking structure of epoxy (Fig. 1.3) [51, 52].

![Diagram of synthesis of reactive carbon nanofiber (re-GNFs)](image)

Graphitic nano-fibers with amino group: GNF-ODA

Oligomer: reactive nano-fibers (re-GNFs) with reactive group –OH*

Fig.1.3 Scheme of synthesis of a reactive carbon nanofiber (re-GNFs)

This special nano-structure of the re-GNFs can be dissolved in reactive epoxy diluent to form a solution of nanofibers in the diluent, which is so-called “liquid nano-reinforcement” (LRN). Due to the compatibility between the molecules of the solution and epoxy (they both have the same epoxide group existing in their structures), the LRN can be easily dispersed in the epoxy resin, and kept in stable state for a long time, essentially indefinitely. In the mean time, the existence of re-GNFs with the reactive group, -OH*, can transform the epoxy into a reactive nano-epoxy. Along with the existence of diluent molecules, the wetting and adhesion properties of the nano-epoxy can be improved, which has been previously observed in an ultrahigh molecular weight polyethylene (UHMWPE) fiber surface [18-20]. The studies also showed that the optimized ratio of 1:6 between the re-GNFs and the BGE diluent can significantly improve wettability of epoxy matrix to UHMWPE fibers [54]. Therefore, the synthesized nanofiber-covalent-epoxy oligomers in liquid format are suitable for structural fiber composite production and possessed great potential for energy efficient RI manufacturing of structural FRP fiber composites with high quality and
1.3 Wetting behaviors of epoxy on the smooth and rough surfaces

In manufacturing a FRP, first the resin matrix should have good wet-out on fiber surface, and then curing reaction occurs to form sufficient adhesion between the matrix and fibers.

Typically, good wetting behavior of polymer matrices can assist better wet-out of matrix to fiber in the fiber lay-ups, effectively reduce dry spots from incomplete wetting in the preform, and finally improve fiber/matrix bonding strength. Therefore, wettability of the matrix material is particularly critical for the manufacturing of high-performance FRP composites.

For a flat homogeneous solid surface a uniquely defined equilibrium contact angle \((\theta_y)\) can be described by Young’s equation (see Equ.1.3) as shown in Fig.1.4; however, for a rough solid surfaces there becomes a complex task to describe the occurring wetting behavior. There typically exists in two prominent states for a drop interacted with a given rough surface. The drop either resides on the peaks of the rough surface or it wets the grooves on the rough surfaces, depending on how it is formed. When the drop sitting on the peaks has air pockets along its contact with the substrate, it will be termed a composite contact. Therefore, there exist two basic theories to describe the two states on the rough surfaces.

\[
\cos(\theta_y) = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
\]  

(1.3)
The widely used theories for studying wetting behaviors on the rough surfaces were established many years ago by Wenzel [55] and Cassie and Baxter (CB) [56]. In Wenzel’s approach it is assumed that the liquid fills up the grooves on the rough surface (Fig. 1.5). A drop on a rough high-energy surface will therefore appear to sink into the surface. The Wenzel equation relates to the homogeneous wetting regime and yields the Wenzel apparent contact angle ($\theta_W$) in terms of the Young contact angle ($\theta_Y$) and the roughness ratio ($r_S$) as described in Equ. 1.4:

$$\cos \theta_W = r_S \cos \theta_Y$$

(1.4)

where the roughness ratio ($r_S$) is defined as the ratio of the true area of the solid surface to its nominal area. For flat surfaces ($r_S = 1$), the Wenzel equation gives the Young’s equation.

From Wenzel’s equation, it can be seen that if the Young’s contact angle of a
liquid on a smooth surface is less than 90°, the apparent contact angle on a rough surface will be smaller, while the Young’s contact angle is larger than 90°, the apparent contact angle on a rough surface will be larger. It means that when the surface is hydrophilic ($\theta_Y < 90°$), the roughness decreases the apparent contact angle; when the surface is hydrophobic ($\theta_Y > 90°$), the roughness increases the apparent contact angle. Therefore, wettability is improved by roughness for a hydrophilic surface ($\theta_W < \theta_Y$ for $\theta < 90º$), but gets worse for a hydrophobic one ($\theta_W > \theta_Y$ for $\theta > 90º$).

In Cassie-Baxter’s approach it is assumed that the liquid forms a composite surface composed of air pockets trapped underneath the liquid and the solid on the rough substrate (Fig.1.6). They proposed that the cosine of the contact angle of a liquid drop on the composite surface corresponds to the sum of the cosines of the contact angles on two homogeneous surfaces of the respective materials.

When one of the surfaces is only air, the cosine of the contact angle on this surface is –1. The CB equation describes the heterogeneous wetting regime and gives the CB apparent contact angle ($\theta_{CB}$) as described in Equ. 1.5

$$\cos \theta_{CB} = r_s f_s \cos \theta_v + f_v \cos \theta_L = r_s f_s \cos \theta_v + f_v - 1$$

(1.5)

Fig. 1.6 Cassie-Baxter State
where \( f_s \) is the fraction of the projected area of the solid surface which is wet by the liquid, and \( r_f \) is the roughness ratio of the wet area. When \( f_s = 1 \), \( r_f = r \), and the CB equation turns into the Wenzel equation.

From Cassie-Baxter’s Equation, it can be found that when the Young’s contact angle is smaller than 90°, the surface roughness will increase the apparent contact angle. This is different from the Wenzel case, because when the intrinsic Young’s contact angle of a liquid on a smooth surface is less than 90°, the apparent contact angle can still be enhanced as a result of the trapped air pockets. For very rough surfaces, for which \( r_S \) will tend to zero, \( \theta_W \) will tend to 180°, and the drop will lift off the solid surface.

As recently realized [57, 58], these equations are necessary but not sufficient conditions for describing wetting equilibrium on rough surfaces. They are correct only if the drop is sufficiently large compared with the typical roughness scale. Generally there is no clear boundary between these two states. On hydrophobic surfaces (\( \theta_Y \sim 100° \)) of moderate roughness, both Wenzel and Cassie–Baxter states may co-exist [59–62].

The sliding-down behavior of a liquid droplet is another criterion for evaluating dynamic wetting behavior of the liquid with the substrate. The sliding behavior of a liquid droplet can be evaluated by measuring the sliding angle on the tilted plate, where a liquid droplet begins to slide down a tilted plate as shown in Fig. 1.7.

The quantitative relationship between the difference between the advancing and receding contact angles (contact angle hysteresis) and the sliding angle (\( \alpha \)) is given by
Equ. 1.6 [63]

\[ \frac{mg \sin \alpha}{w} = \gamma_{lv} (\cos \theta_R - \cos \theta_A) \]  

where \( \theta_A \) and \( \theta_R \) are the advancing and receding contact angles, respectively, \( g \) is the force due to gravity, \( m \) and \( w \) are the mass and width of the droplet, respectively. From Equation, it can be found that a smaller difference between the advancing and receding contact angles will result in a smaller sliding angle.

![Diagram](image)

Fig. 1.7 Wetting behavior of a liquid droplet on the tilted surface

For the two states of a droplet on the rough surface, the Wenzel’s state tends to give a larger difference between the advancing and receding contact angles than the Cassie–Baxter state. Furthermore, in the Wenzel’s state the liquid droplet will stay unmoved on the rough surfaces even if the plate is tilted to a significant angle, whereas it easily rolls off even if the plate is only slightly tilted in the Cassie-Baxter’s state.

### 1.4 Cure kinetics of epoxy modified by nanofillers
In the past decade extensive studies concerning mechanisms and kinetics of epoxy resin cure were presented in literature. The kinetic analysis of pure epoxy resin cure from differential scanning calorimetry (DSC) data reported that the activation energy value was in a wide range of 28~158 kJ/mol [64, 65]. Although variation in activation energy from the kinetic analysis of DSC data appeared to be common, some reports gave approximately constant activation energy value during cure reaction. For example, the study by Bonicelli et al. showed that activation energy remained almost invariable (about 60 kJ/mol) in the whole range of conversions [66]. Yao et al. also found that in the region of 0.3~0.7 for the degree of cure activation energy value was almost a constant. On the other hand, with development of nanocomposites recent studies were also dedicated to understanding the effect of carbon nanofillers on the cure kinetics of epoxy resin [67]. Puglia et al. reported an acceleration effect of single walled CNTs on the cure reaction of the epoxy system using dynamic and isothermal DSC methods [68]. In their study, the decrease of the time reaching heat flow peak were observed as the proof of the acceleration in the early stage of the cure process. Xie et al. [69] also found an acceleration effect of multiple walled CNTs for the cure behavior of epoxy system using isothermal DSC. They conclude that the hydroxyl groups on the surface of the CNTs offered a catalytic effect on epoxy ring opening and were the origin of the modification of the cure behavior. Their studies also found that with an increase of the CNFs content the activation energy decreased in the early stage of the cure reaction. This indicated a very small acceleration effect of CNFs on curing reaction of epoxy resin. However, in the later stage of the reaction, the CNFs
inhibited the curing reaction of epoxy resin [70]. In these investigations, the modification of the cure behavior of epoxy resin from CNTs in the early stage of the reaction was due to surface functional groups on CNTs or catalyst particles.

In contrast with all aforementioned studies, some authors reported a retardation effect of CNTs on the cure reaction of epoxy resin. In their study, the presence of CNTs did not have a significant effect on the total heat of reaction nor on the activation energy compared to pure epoxy [71].

In summary, the effect of unmodified and modified carbon nanofillers on the cure behaviors of an epoxy resin was still inclusive. There were a number of inconsistent conclusions and conflicting explanations proposed in literature results for the reaction mechanisms of epoxy resin system although various authors reported an acceleration effect of CNTs on the cure reaction of epoxy resin.

1.5 Research objectives

Most reported experimental studies on nanocomposites focused on mechanical property enhancement of the composites using higher than 2 wt% CNTs. Whether and how a extremely small amount (< 1 wt%) of GNFs impact the wetting behaviors and curing characteristics of the epoxy resins have rarely been reported, however, such studies will be greatly important for the applications of the nano-modified epoxy resins in FRP composites.

In this study, effects on dynamic wetting behavior and curing behavior of epoxy matrix due to GNFs without and with different functional groups were systematically
examined. By completion of this thesis, we are able to a) address the effects of GNFs without and with different functional groups at extremely low loading levels (< 1 wt%) on the wetting behavior and flowability of an epoxy matrix on the smooth and rough surfaces, thereby gaining an understanding of the underlying reinforcing mechanisms in the property improvement of the nano-modified epoxy FRP composites; b) understand the addition of the re-GNFs on the effects of cure behaviors of epoxy resin and explore the corresponding mathematical model to predict the corresponding kinetic parameter during evolution of cure.

To realize these goals, this thesis is organized into four chapters. Chapter 1 is the introduction of research work including relevant literature review. The background and objectives of this research are summarized in this chapter. Particularly, the fiber/matrix interfacial adhesion problem in advanced FRP composites and state-of-the-art of nanotechnology for advanced structural composite materials are summarized in this chapter. Chapters 2 and 3 report the experimental results of the investigations. Chapter 2 examines the effects of GNFs with and without functional groups on surface tension, contact angle, droplet spreading rate, and viscosity of the epoxy resin systems. Wetting characteristics of the re-GNFs modified epoxy resins on the rough surfaces of the woven fabric are further analyzed. Chapter 3 focuses on the effects of the re-GNFs on curing kinetics studies of the epoxy resin systems. Chapter 4 summarizes the major conclusions of this research and future work.

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2196–2204.
CHAPTER 2 WETTING BEHAVIORS OF CARBON NANOFIBERS MODIFIED EPXYOY RESINS

This section aimed to first present a thorough elucidation of GNFs without and with different functional groups on effects of dynamic wetting behavior of epoxy matrix. On the other hand, to further understand influence of the re-GNFs on epoxy matrix for application in the manufacturing of FRP composites, the wetting behaviors of the re-GNFs modified epoxy resin on the rough fabric surfaces were also examined. In this experiment pure epoxy resin was chosen as a control to clearly elaborate the differences between the re-GNFs modified epoxy and epoxy resin.

2.1 Introduction

Epoxy resin is the most widely used matrix material for structural fiber-reinforced polymer (FRP) composites due to its good processability and exceptional properties [1-4]. In order to meet higher structural performance of FRP composites, the performances of epoxy resin need to be further promoted to match the advanced performance of fiber reinforcements for many applications including aeronautical and aerospace applications. Recently, the rapid development of nano science and technology offers the possibility to produce materials with properties that can not be obtained by traditional means. The use of CNTs or graphitic carbon nanofibers (CNFs or GNFs) as polymer reinforcements is a particularly attractive selection to enhance the material properties of polymer matrices. To date, most experimental studies on the CNTs or CNFs-based composites focused on mechanical property enhancement of the
composites using higher than 2 wt% CNTs. To my knowledge, the effects of GNFs, particularly at an extremely low amount, on the wetting and flow behaviors of the epoxy resins are rarely reported. However, resin wettability and flowability are critically important for achieving high performance composites to manufacture structural FRP composites because the properties of the end FRP composite parts are strongly influenced by the infusion and wetting characteristics of matrix resins during the manufacturing [12].

Fiber reinforced polymer (FRP) composites typically consist of fibers or woven fabric from fibers embedded in a thermosetting resin matrix. Macroscopically, the woven fabric has a coarse textured surface and hence significantly different from the smooth solid surfaces which have been paid attention to in the extensive research. Theoretically, the characteristic and complex geometry of the woven fabric have apparent effects on the initial wetting behavior and the dynamics of wetting of a droplet because as the surface roughness increases, it becomes difficult for the liquid resin to conformally wetting the surface texture. Therefore, understanding wetting on rough surfaces is very essential for designing and controlling wetting processes during manufacturing of advanced FRP composites.

Investigation of dynamic wetting behavior of various GNFs modified epoxy resins can help to exploit the underlying reinforcing mechanisms and understand the property improvement of high-performance epoxy FRP. The knowledge of wetting and flow behavior of epoxy resins modified by GNFs will provide an essential assistance in producing good fiber wetting out and void-free parts and advance the
successful design of the high-performance epoxy FRP composites.

2.2 Experimental

2.2.1 Materials

The EPON 828 epoxy used in the experiments was purchased from Miller-Stephenson. Its basic chemical composition is bisphenol A (BPA) diglycidyl ether. Butyl glycidyl ether (BGE) as reactive diluent was manufactured by Aldrich Chemical Company. Pyrograf®-III graphitic nanofibers (GNFs), and their oxidized derivatives were obtained from Applied Sciences Inc. The structure of oxidized graphitic nanofibers was given in Fig. 2.1. Graphene plate edges exposed on the GNFs surface provide potential reactive sites for introducing other functional groups. With the attachment of 3, 4'-oxydianiline (ODA) linker molecules on their surface, the functionalized graphitic nanofibers (GNF-ODA) were prepared by Vanderbilt University [5, 6].

Fig. 2.1 Structure of ox-GNFs

Fig. 2.2 Reactive graphitic nanofibers in the liquid nano-reinforcement (LNR)
2.2.2 Sample preparation

Employing the functionalized graphitic nanofibers (GNF-ODA) provided by Vanderbilt University, the reactive graphitic nanofibers, re-GNFs with structure shown in Fig. 2.2, were developed by a reaction with BGE under sonication treatment. The details of the synthesized re-GNFs were described in [8, 9]. By controlling the ratio of re-GNFs to BGE (1:6), the liquid nano-reinforcement, LNR, was formed to facilitate the dispersion and reaction of re-GNFs with epoxy resin [7]. The prepared LNR further mixed with epoxy resin to form various modified epoxy samples (named as re-GNFs samples) with 0.2, 0.3, and 0.5 wt% re-GNFs loadings. Our previous study results indicated that the reactive H* of the OH group attached on re-GNFs can lead the nanofibers to be involved in the curing reaction of epoxy resins as curing agents do, and then integrate the nanofibers into the cured epoxy structures.

In comparison, the as-received GNFs (as-GNFs) and oxidized GNFs (ox-GNFs) were added into the epoxy resin, accordingly forming the nano-filled epoxy samples. Similar to the preparation of re-GNFs epoxy samples, as-GNFs, and ox-GNFs were weighed and added into the flasks. Certain amount of acetone solvent was then poured into the flasks containing as-GNFs and ox-GNFs for 3 hours sonication treatment. The detailed sonication processing was described in [9]. After sonication treatment the solvent was fully removed by using a vacuum oven. The dried as-GNFs and ox-GNFs were added into BGE diluent by the ratio of 1:6 (same as that of re-GNFs modified epoxy samples), and finally mixed with the pure epoxy resin to prepare various testing samples with 0.2, 0.3, and 0.5 wt% GNFs loadings. Therefore, all those
nano-modified epoxy samples have relevant BGE since the ratio of nanofibers to BGE is 1:6, i.e. 1.2, 1.8 and 3.0 wt % BGE for the samples with 0.2, 0.3 and 0.5 wt% of GNFs, accordingly. In the experiment the controlled BGE samples with 1.2, 1.8, and 3.0 wt% BGE loading were prepared for comparison studies. The prepared samples were summarized in Table 2.1.

Table 2.1 The prepared epoxy samples

<table>
<thead>
<tr>
<th>Epoxy sample description</th>
<th>Group 1 GNFs/BGE</th>
<th>Group 2 GNFs/BGE</th>
<th>Group 3 GNFs/BGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-GNFs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(as-GNFs+BGE+epoxy)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ox-GNFs</td>
<td>0.2 wt%/1.2 wt%</td>
<td>0.3 wt%/1.8 wt%</td>
<td>0.5 wt%/3.0 wt%</td>
</tr>
<tr>
<td>(ox-GNFs+BGE+epoxy)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>re-GNFs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(re-GNFs+BGE+epoxy)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Controlled samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(BGE+epoxy)</td>
<td>1.2 wt% BGE</td>
<td>1.8 wt% BGE</td>
<td>3.0 wt% BGE</td>
</tr>
</tbody>
</table>

Note: Ratio of nanofibers: BGE = 1:6

2.3 Measurements

a) Viscosity

The viscosity for all formulations was performed on a Brookfield Model DV-I Prime Digital Viscometer with the spindle and small sample adaptor (SC4-29/13R) at 25±1 °C. The spindle was rotated in the testing samples with a shear rate of 20 rpm for 1 min before a reading was recorded for temperature equilibration. Each formulation was repeated ten times and their average value was taken to be the viscosity of the testing samples.

b). Surface tension—Du Nouy ring method
Du Nouy ring method was applied to measure the surface tension of prepared epoxy samples. This method utilizes a platinum-iridium alloy ring with a well-defined geometry to pull through the testing liquid surface and their surface tension value is then determined. In the experiments the Pt-Ir alloy ring was hung on a DCA microbalance, then submerged below the testing liquid surface, and finally raised upwards as the stage moved upward and downward. The pull forces were recorded by the microbalance as the ring interacted with the liquid surface. Due to high energy surfaces of the Pt-Ir ring, the complete wetting occurred between testing liquid and the ring and the contact angle between testing liquid and the ring hence insured to be zero. The recorded pull forces can be used to calculate surface tension of the testing liquid.

In each of our experiments a beaker with 40ml epoxy samples was placed on the stage for measurement. Before each measurement the testing samples should be stirred to obtain the fresh liquid surface and further degassed to remove the generated bubbles in the solutions. During the measurements, all samples were kept at a constant temperature. Before each testing, platinum-iridium ring and the used solid probes such as cover glasses needed to be gently flamed by a propane torch to remove surface contaminants and residues. During the experiments the ring must be accurately parallel to the surface of the testing liquid. Each sample was repeated five times and their average value was considered to be the final surface tension of the testing sample.
c) Contact angle

Numerous methods can be chosen to measure contact angles such as capillary rise, captive bubble, Wilhelmy balance, laser goniometry, and so on. Generally they were divided into two types. One type is called static testing mode and the other is dynamic testing mode. The static testing mode measures the contact angle at the solid/liquid interface, which is not in motion. The dynamic testing mode measures the contact angle of the liquid in motion with respect to the solid surface. In our experiments the Wilhelmy technique is used to characterize the dynamic contact angle of epoxy samples.

All DCA measurements were carried out with a Calm DCA Model 322 analyzer (Cerritos, CA), which is based on Wilhelmy technique. Motor and balance calibration were performed prior to each testing. A stage speed of 10µm/s with advancing and receding motions of 4 mm was used with all testing specimens. For a comparably slow velocity of the immersion and withdrawal, the dynamic effects on the wetting forces are supposed to be negligible. The top and bottom dwell times were zero second. The final advancing contact angle is taken from the average of the repeated five measurements.

A schematic illustration of the Wilhelmy method is shown in Fig. 2.3. The wetting force $F$ required to pull a solid probe into a liquid is given as Equ. 2.1:

$$F_p = \gamma_L P \cos \theta - \rho_L g Ah$$

(2.1)

where $P$ is the wetted perimeter of the solid probe, $\gamma_L$ is the surface tension of the testing liquid, $\theta$ is the liquid-solid contact angles, $\rho_L$ is the testing liquid density, $A$ is
the cross-sectional area of the solid plate, \( h \) is the immersion depth, and \( g \) is the gravitational constant. As shown in Equ. 2.5, when a plate just touches a liquid surface, i.e. \( h = 0 \), and \( F \) is measured, when the surface tension of the liquid and perimeter of the plate are known, the contact angle can be determined by this equation.

\[
\cos \theta = \frac{\cos \theta_a - F_r}{\gamma \times p}
\]

\[
\cos \theta = \frac{\cos \theta_a - F_a}{\gamma \times p}
\]

Fig. 2.3 Typical plot of pull forces vs. immersion depth of Wilhelmy method during one test cycle (\( \theta_a \): advancing contact angle; \( \theta_r \): receding contact angle)

d) Wetting behavior analysis on the smooth and rough surfaces

A VCA Optima Analyser (AST Products, Billerica, MA, USA) was used to characterize spreading rate of the prepared epoxy samples with glass substrates by the static contact angle measurement. Before the measurements the samples were stirred by a glass rod to keep the fresh surface. Liquid drops of 5µl from each solution were
set to make the measurement. Photographs of the drops were taken at 10 frame/s for 1 min by the video camera of the contact analyzer after a short waiting period of 1s.

2.4 Results and discussion

2.4.1 Wetting behavior of carbon nanofibers modified epoxy on the smooth surfaces

a) Viscosity

In the manufacturing of FRP composites good flowability of polymer matrix is generally required for efficiency of resin infusion. Lower viscosity of polymer matrix implies good flowability and can minimize energy consumption to infiltrate into the preform for matrix. Furthermore, viscosity of polymer matrix affected the spreading behavior of polymer matrix on the fiber reinforcement surface, controlled diffusion and penetration process into the preform, and ultimately determined the performance of the end products. Therefore, the viscosity of the polymer matrix was an important index for characterizing wetting behavior of matrix resin.

In the experiments, we found that viscosity values of all epoxy samples fluctuated with the surrounding temperature variation, even as little as 0.5 °C change. However, the percentage of all epoxy samples over pure epoxy samples kept relatively stable. Therefore, in the experiments the percentage of all testing samples over pure epoxy was taken to represent relative viscosity values of the testing samples instead of their real viscosity values. The decreasing percentage of viscosity over pure epoxy for the different groups of epoxy samples was listed in Table 2.2.

Of all the GNFs modified epoxy samples, the re-GNFs epoxy samples showed the highest decreasing percentage of viscosity and only slightly lower values than the
corresponding controlled BGE samples. The as-received GNFs epoxy samples had the minimum decreasing percentage of viscosity and the ox-GNFs samples with 0.5 wt% ox-GNFs loadings gave higher decreasing percentage of viscosity than those of as-GNFs epoxy samples with the same nanofiber loading. The experimental results revealed that the different types of nanofibers led to different viscosity decreasing of epoxy resin. The re-GNFs contributed to larger viscosity decreasing over the oxidized and as-received GNFs because the reactive group in the re-GNFs led to the strongest interactions with epoxy, chemical bonding between GNFs and epoxy compared to the as-GNFs and ox-GNFs samples.

Under low concentrations of GNFs, the more the amount of GNFs in the epoxy samples, the higher decreasing percentage of viscosity over epoxy. The decreasing viscosity of epoxy matrix is of practical importance for resin infusion processing. The lower viscosity can promote resin flow in the mold and allow thick parts to be easily permeated with less energy consumption under the smaller driving force of vacuum and/or external pressure.

Table 2.2 Decreasing percentage of viscosity over pure epoxy

<table>
<thead>
<tr>
<th>Epoxy samples</th>
<th>Group 1 (GNFs/BGE)</th>
<th>Group 2 (GNFs/BGE)</th>
<th>Group 3 (GNFs/BGE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 wt%/1.2 wt%</td>
<td>0.3 wt%/1.8 wt%</td>
<td>0.5 wt%/3.0 wt%</td>
</tr>
<tr>
<td>as-GNFs</td>
<td>40.6%</td>
<td>52.5%</td>
<td>60.8%</td>
</tr>
<tr>
<td>ox-GNFs</td>
<td>40.7%</td>
<td>52.6%</td>
<td>65.8%</td>
</tr>
<tr>
<td><strong>re-GNFs</strong></td>
<td><strong>45.7%</strong></td>
<td><strong>53.7%</strong></td>
<td><strong>67.1%</strong></td>
</tr>
<tr>
<td>controlled</td>
<td>46.5%</td>
<td>53.5%</td>
<td>70.3%</td>
</tr>
</tbody>
</table>
b) Surface tension

In surface tension measurement the recorded wetting force changed with the increase and decrease of the immerse depth. A typical pull force-displacement curve from a testing cycle is shown in Fig. 2.4. In the initial stage as the ring hit the liquid surface, a slightly positive force was observed due to the interaction force between the ring and the liquid surface. The ring then pulled through the liquid surface and produced a negative force from the liquid surface tension. With the formation of the supporting wire on the ring, a small positive force was recorded. As the stage moved downward and the ring broke through the surface, the pull force started to increase. As the stage moved on, the measured force continued to increase to reach its maximum. Then it began to decrease until the formed lamella fully broke.

Fig. 2.4 Typical force-displacement curve from the test cycling

Two pull forces, the break force and the maximum force, can be generally chosen to calculate the surface tension of testing liquid as shown in Fig. 2.5. Based on the
recorded pull force, the surface tension values of the testing liquid can be obtained from Eqn. 2.2.

\[ \gamma = \frac{F_{\text{measured}}}{2 \times C} \times f \]  \hspace{1cm} (2.2)

where \( F_{\text{measured}} = F_{\text{max}} \) or \( F_{\text{break}} \), \( C \) is the circumference of the metal ring, and \( f \) is the correction factor.

![Fig. 2.5 Pull force versus displacement in the test cycling](image)

Obviously, the maximum pull force gives higher surface tension values than those from the breaking pull force. In the measurement, a shape correction factor is applied. Because the size and shape of the inside and outside of the ring are hard to guarantee the same, the measured results are hence corrected according to Eqn. 2.3.

\[ P = 4\pi r_m \gamma_L \]

\[ \gamma_f = f \gamma_L \]  \hspace{1cm} (2.3)
where $P$ is the total pull force on the ring, $r_m$ is the mean radius of the ring, $\gamma_L$ is the liquid surface tension, and $f$ is the shape corrector factor.

In the experiment, two different pull forces were first used to calculate surface tension of the controlled BGE samples. We found that surface tension values calculated from the maximum pull force (DIN standard) gave a large variation in the measurements, the range of 10 mN/m, however, surface tension values calculated from the breaking force had relative steady values. Furthermore, the fresh testing liquid/air interface related to the breaking force may be easily created, thereby minimizing effects of GNFs agglomeration on the experimental results. Therefore, the breaking force (ASTM) was selected to calculate surface tension values of the epoxy samples in the following experiments.

The experimental results of pure epoxy and the prepared epoxy samples were reported in Fig. 2.6. It was shown that surface tension of pure epoxy, 41.89 mN/m, was the highest one among all epoxy samples. With addition of BGE diluent and combination of BGE and different nanofibers, surface tension decreased. The errors ranged from 0.1 to 0.5 mN/m, which were insignificant for the experimental results. The previous work confirmed that BGE diluent may decrease surface tension of epoxy resin [9]. With the incorporation of nanofibers into epoxy matrix, a larger decrease was found in all nanofiber modified epoxy samples. This was possibly due to the interactions between the GNFs and epoxy. Compared to the as-GNFs epoxy samples, ox-GNFs, and re-GNFs epoxy samples had more pronounced decreases in surface tension due to their stronger interaction with epoxy molecules. The
pronounced decreases in surface tension were because, through surface oxidization and functionalization of GNFs, some active functional groups were attached to the GNFs surface and these active functional groups improved interactions with epoxy molecules. In particular, the liquid nano-reinforcement (LNR) formed from the re-GNFs gave the smallest surface tension values in the epoxy samples. Covalent bonding between the re-GNFs and epoxy matrix made the LNR effectively disperse in the epoxy resins and stabilized for a long time, approximately infinite [7]. The integrated stable epoxy system can effectively decrease surface tension of epoxy matrix. The reduction in surface tension of epoxy matrices can predict good wettability with various fiber reinforcements and offer possibility in interfacial properties improvement of epoxy and fiber reinforcements.

![Surface tension of pure epoxy, controlled BGE epoxy, and nano-modified epoxy samples](image)

Fig. 2.6 Surface tension of pure epoxy, controlled BGE epoxy, and nano-modified epoxy samples
c) Dynamic contact angle

Figure 2.7 represents the measured advancing contact angles of all epoxy samples from dynamic wetting experiments. Compared to pure epoxy samples, all the modified epoxy samples including the BGE controlled samples showed reduced advancing contact angles, which are due to the fact that all these samples have BGE diluent. However, compared to the counterpart of the BGE controlled samples, the samples with as-GNFs and ox-GNFs showed increased advancing contact angles; only re-GNFs epoxy samples showed lower advancing contact angles than the BGE controlled samples. For the as-GNFs and ox-GNFs epoxy samples, larger advancing contact angles than those of the controlled samples, which is inconsistent with surface tension experiments, indicated that nanofibers contributed to nonlinear effects on advancing contact angles in the nano-modified samples.

For the re-GNFs epoxy samples, a consistent observation with surface tension was found in the experiments, and all the three re-GNFs epoxy samples showed lower contact angles than the BGE controlled samples accordingly. This fact confirmed that the re-GNFs modified epoxy (which was called “nano-epoxy” in our previous studies [9]) has the special wettability due to the re-GNFs materials, which have dramatic contribution to the wettability for the resulting nano-modified epoxy system. More distinct decreases in advancing contact angles were achieved in the samples with 0.3 wt% and 0.5 wt% re-GNFs. For example, for 0.3 wt% re-GNFs epoxy samples, there existed an approximately 15% drops in advancing contact angles over the BGE controlled sample, and 25% drop over the pure epoxy sample. The distinct reduction
in the advancing contact angles for the re-GNFs samples resulted from the decrease of surface tension that is related to the formation of the strong interaction between the re-GNFs and epoxy. It was indicated that with introduction of the re-GNFs, the novel epoxy matrix was developed and it was fully different from simple mixture of the conventional epoxy nanocomposites [5, 9].

![Graph showing advancing contact angles of various epoxy samples](image)

Fig. 2.7 Advancing contact angle of pure epoxy, controlled BGE, and nanomodified epoxy samples

d) Wetting behavior analysis on the smooth surfaces

Figure 2.8 shows droplet spreading behavior of various epoxy samples on smooth glass substrate. In the measurement each type of samples was repeated five times and the average value of their readings was taken to be the final testing result. The standard deviation of the testing results was below 1.2 mPa·s. From the experimental results shown in Fig. 2.8, we found that in the initial stage a quick drop of static contact angles within 2 seconds was observed for all samples. As time
elapsed, changes of the static contact angles became slow and the curves gradually tended to became stable. Finally, after about 30 seconds the static contact angle changes leveled off and reached the steady values.

Compared with pure epoxy samples, all those nano-modified epoxy samples and BGE controlled samples showed faster decrease of the contact angles with elapsed time. The faster decrease in the contact angles within short time demonstrated good spreading behavior. Among all samples the re-GNFs epoxy samples had the lowest static contact angles in the final stage and the fastest spreading rate among those nano-modified samples though except the controlled BGE samples. In particular, the re-GNFs samples showed very different spreading characteristics i.e. a continuous decrease, from all other samples that reached the steady spreading rates at the 20 seconds. The smaller static equilibrium contact angle was finally obtained within a relatively longer time for this re-GNFs epoxy samples.

The observations of spreading behavior of the re-GNFs modified epoxy samples were fully in agreement with the results of advancing contact angle in the dynamic contact angle experiments. These results confirmed that the re-GNFs effectively enhanced wetting behavior of epoxy resin than the other two types of nanofibers, as-GNFs and ox-GNFs. Furthermore, the continuously decreasing spreading behavior of the re-GNFs modified epoxy is particularly significant for resin infusion processing, such as vacuum assisted resin transfer molding (VARTM) technology. It will aid the fiber reinforcement wet-out and reduce the formation of dry spots in the manufacturing of FRP materials, also, fast spreading rate than the pure epoxy resin
can make the resin infusion processing reduce the need for pressure used to infuse the resin into the fiber preform. In result, this re-GNFs modified resin will make the FRP composite manufacturing energy and cost efficient. Therefore, the developed re-GNFs approach is a more effective for enhanced wettability of matrix.

![Graph](image_url)

Fig. 2.8 Wetting behavior of pure epoxy, controlled epoxy with BGE, as-GNFs, ox-GNFs, and re-GNFs epoxy samples

Based on the experimental results, the spreading rate can be expressed as a decreasing function of contact angles as expressed in Equ. 2.4:

\[
\frac{d\theta}{dt} = -K\theta
\]

(2.4)

where \( \theta \) was the contact angle at a particular time, \( K \) was the spreading rate constant and represented the relative contact angle decreasing rate.
As droplet spreading proceeded on the smooth glass surface, spreading rate decreased and finally reached an equilibrium contact angle at infinite time. Therefore, the spreading model of contact angle with time became Equ. 2.5

\[
\theta = \theta_0 e^{-kt} + \theta_e
\]  

(2.5)

where \( \theta_0 \) was an initial contact angle parameter, \( \theta_e \) was the equilibrium contact angle.

The spreading model was applied to fit the experimental data and determined the corresponding \( K \)-constant, the initial contact angle, and the equilibrium contact angle. Based on the model expression, the \( K \)-constant may be used to quantify the spreading rate of all epoxy samples. The higher the \( K \)-constant, the faster the contact angle reached the final steady state and the larger the spreading rate. When \( K \) was larger than a critical value, instant wetting with the solid surface occurred.

The nonlinear curve-fitting results were listed in Table 2.3. As seen in Table 2.3, the adjusted R-squared values were over 95% for most of types of epoxy samples tested. Among all samples, BGE samples exhibited the greatest \( K \)-constant value. Another larger \( K \)-constant value was found in re-GNFs samples. Although ox-GNFs samples had a similar \( K \)-constant value to re-GNFs samples, a lower equilibrium contact angle was observed in re-GNFs samples. The larger \( K \)-value and lower equilibrium contact angle of the re-GNFs samples indicated their good spreading properties. Therefore, the spreading model can be used to characterize the spreading process on the smooth surface.
The geometrical evolution of the droplets in the spreading process on the smooth glass surface is shown in Fig. 2.9. When liquid droplets fell from the needle, the droplets from different types of epoxy samples exhibited different geometric shapes. In the pure epoxy and as-GNFs samples the approximate ellipsoidal geometry was observed in the experiments, however, in BGE, ox-GNFs, and re-GNFs epoxy samples, the prolate spheroid shape was apparent with different lengths of the major axis. The difference of geometric shapes at the starting moment originated from the difference of spreading properties and viscosity in these samples. With the elapse of time, the oblate spheroid shape with different lengths of major axis was seen from various epoxy samples at the same particular moment. At the equilibrium state, the largest length of major axis of the oblate shape was observed from the re-GNFs samples. The geometric shape evolution of the droplets from different epoxy samples during the spreading process offered directly perceived evidence that different types of nanofibers led to different wetting behavior of epoxy resin. Particularly, re-GNFs
samples possessed faster spreading rate and minimum equilibrate contact angle than the other nanofiber filled systems.

Fig. 2.9 Evolution of droplet geometric shapes of various epoxy samples (Row 1: re-GNFs; Row 2: ox-GNFs; Row 3: as- GNFs; Row 4: BGE; Row 5: pure epoxy)

2.4.2 Wetting behavior of carbon nanofibers modified epoxy on rough fabric surfaces

The glass fiber-woven and PE fiber-woven mats with the different surface roughness were used in the experiments to study wetting behavior of the re-GNFs modified epoxy on the rough substrates. The difference of surface roughness between the two woven mats originated from the difference of structures of the fiber reinforcements and the processing of the woven mats as shown in Fig. 2.10. Wetting behaviors of the re-GNFs modified epoxy on the glass fiber fabric and PE fiber fabric surfaces were evaluated by the contact angle experiments. As shown in Fig. 2.11 and...
Fig. 2.12, the re-GNFs modified epoxy matrix had significantly different wetting characteristic on these fabric surfaces from pure epoxy matrix. It was seen that the re-GNFs modified epoxy quickly spread and easily filled up the grooves on these rough fabric surfaces and hence showed a zigzag-like contact line on the rough fabric surfaces. However, the droplets of pure epoxy sat on the top of these rough fabric surfaces without filling up the grooves of the woven fibers so that air was enclosed between the droplet and the fabric substrate. This is similar to the Cassie-Baxter’s state. So the entrapped air pockets were observed in the region of the contact lines on the two substrates for pure epoxy. The re-GNFs modified epoxy exhibited good spreading on the rough fabric surfaces and penetration into the micro-rough structures and produced sufficient wetting behavior for the fabric surfaces. This behavior is the same as the Wenzel’s state. Due to fill-up and penetration of the re-GNFs modified epoxy into the grooves of the rough surfaces, no trapped air pockets were found in the region of the contact lines on the two substrates. Thus, an apparently closed contact area between the droplet and the substrate for the re-GNFs modified epoxy is found in the images. Based on the experimental observation, the droplets of the re-GNFs modified epoxy exhibited the wet contact to the rough fabric surfaces and formed a quasi-continuous contact line close pinned to the surfaces; however, the droplets of pure epoxy presented a composite contact. With the air pockets trapped in the grooves the dry contact finally resulted in a discontinuous contact line. This discontinuous contact made it easy for the droplets to roll off the rough surface. The good spreading and easy penetration of the re-GNFs modified epoxy was due to the reduced viscosity.
compared to pure epoxy. The lower viscosity of the re-GNFs modified epoxy contributed to good flowability and spreading behaviors on the rough surface and at the same time the roughness of the substrate further magnified the difference of wetting behaviors between the modified epoxy and pure epoxy based on the Wenzel’s and Cassie-Baxter’s theories. Therefore, a significantly different wetting behavior was observed in the experiments.

Fig. 2.10 Surface morphology of the glass fiber woven and PE fiber woven mat surfaces
Fig. 2.11 Dynamic wetting behaviors of pure epoxy and re-GNFs modified epoxy on the glass fiber woven fabric surfaces.

Fig. 2.12 Dynamic wetting behaviors of pure epoxy and re-GNFs modified epoxy on the PE woven fabric surfaces.
As comparison, wetting behaviors of the re-GNFs modified epoxy and pure epoxy samples on the smooth surfaces were give in Fig. 2.13 and Fig. 2.14. It can be seen that although variations in geometric shapes and contact angle between two systems were observed in the smooth surfaces, it did not fully reflect the difference in the practical application because in reality fewer solid surfaces are truly smooth. This difference in wetting state of two epoxy systems on the rough fabric surfaces was fully reflected influence of addition of the re-GNFs into epoxy resin.

Fig. 2.13 Evolution of droplet geometric shapes of epoxy samples
Figure 2.15 developed a dry-wet contact model to illustrate different wetting mechanisms of pure and re-GNFs modified epoxy on the rough fabric surfaces based on the theory of the apparent contact angles. According to the relations of surface roughness with contact angle, for the Wenzel’s case if contact angle on a smooth surface is less than 90°, the apparent contact angle on the rough surface will become smaller; however, for the Cassier-Baxter’s state, the surface roughness will increase the apparent contact angle. This implies that for Wenzel states hydrophilicity will be more hydrophilic on the rough surfaces. So, the improved wetting behavior of the re-GNFs modified epoxy can be further magnified by the rough fabric surfaces. Furthermore, in the experiments no trapped air pockets were found in the region of the
contact lines and the continuous contact lines were obtained in the images for the re-GNFs modified epoxy samples. It has been recognized that with the infusion of matrix resin into the preform the air pockets can be trapped and hence contribute to the source of dry pots for FRP laminates. These dry spots will finally lead to insufficient wetting behavior of matrix resin onto the fiber reinforcements and finally produce local voids of the FRP laminate. This may greatly degrade the strength of FRP composites. The experimental results indicated that the re-GNFs modified epoxy avoid the air pockets trapped in the fabric preform by their sufficient wetting and fast penetration. Importantly, the dry-wet contact model further manifested the difference of dynamic spreading of two systems on the fabric surfaces can be manifested by the dry-wet contact model, but can not be characterized by the basic models of Wenzel’s state and Cassie-Baxter’s state. Therefore, it can be concluded that the enhanced wetting behavior of the re-GNFs modified epoxy particularly possessed the practical importance on the manufacturing of the FRP composites.

![Dry and Wet Contact](image)

**Fig. 2.15** Wetting behavior on the rough surface for pure and re-GNFs modified epoxy (Dry-wet contact model)

When the droplets of the re-GNFs modified epoxy started to slide down the tilted
plate of the glass fiber woven mats, their wet contact lines also forwarded as shown in Fig. 2.16. The liquid resin was conformably filled in the woven fabric texture initially, however, when the wet contact lines receded, some liquid resin can be trapped in the woven surface texture. This dynamic wetting behavior can significantly decrease the receding contact angle and result in a large contact angle hysteresis and thus in a large critical sliding angle the larger sliding angle increases difficulty for the droplets to roll off from the rough surfaces. The liquid resin trapped in the surface texture was not observed for pure epoxy samples; the contact angle hysteresis and critical sliding contact angle were much smaller than the re-GNFs modified epoxy. In other words, the droplets of pure epoxy rolled off easily on the rough fabric surfaces. Among various possible mechanisms, it has been shown that the poor continuity of the contact lines (dry contact state) from pure epoxy are most preferable to give a low critical sliding angle and make them slide down easily on the rough tilted fabric surfaces. This wetting behavior was further verified by the images of optical microscopy in the investigation of dynamic spreading as shown in Fig. 2.17. The re-GNFs modified epoxy showed good and fast spreading behavior on the rough fabric surfaces. In the image the flow fronts of the re-GNFs modified epoxy exhibited convex, a tendency to facilitate the spreading, however, in the image of pure epoxy sample the concave flow fronts were observed. The difference of the flowability on the rough fabric surfaces contributed to the difference of viscosity and wetting characteristics of the two types of matrix resins. The good flowability of the re-GNFs modified epoxy can not only save time of resin infusion, but also reduce energy consumption during the
manufacturing of FRP composites. Therefore, the re-GNFs modified epoxy is of practical importance for resin infusion processing.

Fig. 2.16 Dynamic wetting behavior on the tilted rough surface glass fiber fabric surface

Fig. 2.17 Spreading behavior on the rough glass fiber fabric surface (20X) from two systems (Arrow: moving direction of fluid)
2.5 Conclusions

Wetting behaviors of the different nanofiber modified epoxy matrices were studied by using various measurement techniques including viscosity, contact angle, surface tension, spreading rate, and sliding angle on the tilted surface, etc. The results showed that the addition of even a small amount of carbon nanofibers affected wetting behaviors of epoxy resin, particularly on the rough fabric surfaces. Specifically, the re-GNFs modified epoxy led to the lower surface tension, the lowest advancing contact angle, the fastest spreading rate, and the biggest decreasing rate of viscosity among all nano-modified epoxy samples. The advancing contact angles of the re-GNFs epoxy samples are even lower than those of the BGE controlled epoxy samples. Furthermore, the re-GNFs possessed the reduced viscosity significantly different from viscosity enhancement in the nanocomposites.

This is the first time to obtain images of wetting behavior of epoxy resins on fabric surfaces in labs. The experimental observation showed that the basic models developed by Wenzel and Cassier-Baxter may be used to explain the observed difference in wetting behaviors between pure epoxy and re-GNFs modified epoxy resins on the horizontal fabric surfaces. Furthermore, a dry-wet contact model was developed to characterize the significantly different behaviors of dynamic wetting processes between pure epoxy and re-GNFs modified epoxy resins on the horizontal and tilted fabric surfaces, which can not be represented by Wenzel and Cassier-Baxter models. The re-GNFs modified epoxy resin has been shown to have unique wetting
and flow behavior, which is significant for its application in FRP manufacturing as the matrix material.

References


CHAPTER 3 CURING KINTERICS OF RE-GNF MODIFIED EPOXY MATRICES

In this section, the effect of the re-GNFs on the curing behavior of an epoxy resin was studied using non-isothermal DSC method.

3.1 Introduction

It is known that the physical and mechanical properties of the cured epoxy resins are dependant on their structures, the extent of curing, the curing conditions, and the time and temperature of curing. Therefore, for epoxy resins, the extent of curing conversion and kinetic parameters are particularly critical for the design of the manufacturing process and the performance of the end products. On the other hand, during the curing process the occurred chemical reactions strongly influence resin morphology and rheological properties. The morphology of epoxy network depends on the relative reaction rate of epoxide with amine so the relative reaction rate is a vital parameter of achieving the information about network structure. Therefore, the study of curing kinetics is beneficial to understand the relationship between the networks of the microscopic structures and the macroscopic performances of nano-modified FRP composites. Additionally, the addition of carbon nanofibers also complicates the curing process of resin matrix. In particular, the processing behaviors of matrix materials with carbon nanofibers are different from those of polymer matrix apparently. The understanding of the curing behaviors of the nano-modified epoxy matrices can contribute to the design of the manufacturing parameters for the resulting
composite parts, which is critical for obtaining the optimized performance of the final products correlated with the structures of polymer network.

Despite the considerable current research efforts in the field of epoxy resin cure, numerous issues have yet to be addressed. For example, whether and how GNFs with functional groups influenced the cure process of epoxy resin. This section attempted to provide an in-depth understanding of the effects of the developed re-GNFs on curing behaviors of the epoxy matrix system and provide guidance for the proper selection of processing parameters. A particular emphasis was given to develop the corresponding mathematical model to elaborate the influence of the re-GNFs on the vitrification phenomena of epoxy system. An appropriate cure kinetic model can help to predict the cure behavior of epoxy resin for process design and control the cure process, thereby allowing a more rational choice of processing conditions and optimizing fabrication process.

To characterize the effects of re-GNFs on the cure kinetics of epoxy resin, one of the most widely used methods is thermal analysis by DSC in isothermal or dynamic mode. Among modes Dynamic method, which is carried out at different heating rates, is a simpler and faster measure to evaluate the curing kinetic parameters because the kinetic data can be obtained in a relatively short period of time. Its disadvantage is some complications in the mathematical analysis of the temperature integral which are inherent to the dynamic mode. The dynamic mode of multiple dynamic temperature scans has been applied extensively in the study of the curing reactions of thermosetting polymers [1-3].
3.2 Kinetic models

In DSC a basic assumption for cure kinetics is that heat flow \( (dH/dt) \) relative to the instrumental baseline is proportional to the cure reaction rate \( (da/dt) \). In the temperature scanning experiments the heat capacity of the sample contributes to the heat flow, and this is compensated by the use of an appropriate baseline under the exothermic or endothermic peak produced by the reaction. A typical DSC scan for an exothermic cure reaction is shown schematically in Fig. 3.1.

![Fig. 3.1 A typical DSC curve for an exothermic cure reaction](image)

In order to determine the evolution of the epoxy cure for modeling, the degree of cure at a given temperature \( (\alpha) \) can be expressed as Equ. 3.1:

\[
\alpha = \frac{A_T}{A_0} = \frac{H_T}{H_0}
\]  

(3.1)

where \( A_0 \) is the total area between the exothermal cure and the baseline, \( A_T \) is the area between the exothermal cure and the baseline at a given temperature (T), \( H_0 \) is the
total heat of the reaction during the whole cure reaction, $H_T$ is the heat of the reaction of partially cured samples at a given temperature (T).

The rate of conversion $d\alpha/dt$ at a given temperature $T$ can be given as Equ. 3.2:

$$\frac{d\alpha}{dt} = \frac{dH/\alpha}{H_0}$$  \hspace{1cm} (3.2)

Without knowing the exact reaction mechanism, it is reasonable to assume that the reaction rate at a given time is only a function of the conversion fraction ($\alpha$) [4]. A general expression often used in the analysis of DSC kinetic data [5] is

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$  \hspace{1cm} (3.3)

where at a given time and temperature $f(\alpha)$ is some function of the fractional conversion ($\alpha$) and $d\alpha/dt$ is the rate of conversion. The apparent rate constant ($k$) is dependent on temperature and usually assumed to be of the Arrhenius form:

$$k(T) = A \exp \left(-\frac{E}{RT}\right)$$  \hspace{1cm} (3.4)

where $A$ is a constant, $R$ is the gas constant (8.31 J/mol K), $E$ is the apparent activation energy, and $T$ is the absolute temperature.

With the assumed Arrhenius equation the rate constant $k(T)$ is introduced and gives

$$\frac{d\alpha}{dt} = A \exp \left(-\frac{E}{RT}\right)f(\alpha)$$  \hspace{1cm} (3.5)

For nonisothermal DSC tests of thermosetting resin cure, the kinetic parameters can be determined from multiple heating rate scans. By the proper transformation, the above equation becomes

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp \left(-\frac{E}{RT}\right)f(\alpha)$$  \hspace{1cm} (3.6)
where $\beta = dT/dt$ is a constant heating rate.

From Equ. 3.6, it is seen that this equation has no exact analytical solution. Therefore, some necessary mathematical methods have been developed to deal with it so that the corresponding kinetic behaviors of cure reaction can be described.

Kinetic analysis of non-isothermal resin-cured system can be performed by the multiple heating rates. A multiple heating rates method, which is called isoconversional method, provides a good example to produce reliable kinetic parameters as well as to accomplish agreement with isothermal conditions. Two kinetic methods widely used to study dynamic kinetics of thermosetting polymers are model-fitting and model-free methods [6-10].

In the model fitting methods for simple reactions the nth order and the autocatalytic models are commonly used. Taking $f(\alpha) = (1-\alpha)^n$ and $f(\alpha) = \alpha^m(1-\alpha)^n$ for cure reaction, Equ. 3.6 can be rearranged into Equ. 3.7 and 3.8, respectively:

$$
\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n\ln(1-\alpha) - \frac{E}{RT}
$$

(3.7)

$$
\ln\left(\frac{d\alpha}{dt}\right) = \ln A + m\ln(\alpha) + n\ln(1-\alpha) - \frac{E}{RT}
$$

(3.8)

From one DSC dynamic scan, the values of $\alpha$ and $d\alpha/dt$ and corresponding temperature $T$ are used to solve Equ. 3.7 and Equ. 3.8 using multiple linear regression. A big disadvantage of this method is that the particular kinetic models have to be first assumed, however, for an unknown system, this assumed prerequisite is problematic.

If the kinetic function ($f(\alpha)$) is not assumed first and is unknown and Equ. 3.3 and Equ. 3.4 apply, the apparent activation energy may be determined. From DSC scans at differing heating rates a series of values of reaction rate ($\beta$) and temperature ($T$) can
be obtained at fixed $\alpha$. The apparent activation energy is then given by

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E}{RT_\alpha}$$

(3.9)

where $\ln[Af(\alpha)]$ is constant for a given conversion ($\alpha$). The value of $\ln[Af(\alpha)]$ can be obtained from the known values of $\ln[da/dt]$ and $E_a/RT$. If the reaction mechanism is of the nth-order kinetics, the intercept is the natural logarithm of the frequency factor and the slope gives the reaction order. This is called the Friedman method. This equation can also be applied to isothermal data obtained at different temperatures.

A relationship between the peak maximum temperature ($T_p$) and $E$ for data obtained at different heating rates was derived by Kissinger [7]:

$$\frac{d\ln(\beta)}{d(1/T_p)} = -\frac{E}{R} - 2T_p$$

(3.10)

The linear relationship between the $\ln\beta$ and $1/T_p$ of the exothermic curing reaction allows us to determine the activation energy of curing kinetics.

Another type of method for the analysis of data from temperature scans at constant heating rate is based on Equ. 3.6 and takes integral form on both sides:

$$\int_0^\infty \frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) \int_{T_0}^T$$

(3.11)

which may be still written as

$$\log F(\alpha) = \frac{A}{\beta} G(T)$$

(3.12)

The right-hand side of Eq. 3.11 can be reduced to an exponential integral by substituting $x=E/RT$ to give

$$G(T) = \frac{AE}{\beta R} p(x)$$

(3.13)
where

\[ p(x) = - \int_{x_0}^{x} e^{-x} / x^2 \, dx \]  \hspace{1cm} (3.14)

Many methods have been devised for the application of Equ. 3.11 to 3.14 to DSC data which involve various approximations of the exponential integral, \( p(x) \). The widely accepted examples are the methods of Doyle and Ozawa [7].

By taking Doyle's approximation for \( p(x) \) in Equ. 3.12 and 3.13, Ozawa obtained the approximate relationship

\[ \ln \beta = \ln \left( \frac{AE_\alpha}{R} \right) - \ln F(\alpha) - 5.331 - 1.052 \frac{E_\alpha}{RT} \]  \hspace{1cm} (3.15)

where \( E_\alpha \) is constant for a given conversion. This is usually sued Flynn–Wall–Ozawa method. Thus, for a constant \( \alpha \), the plot of \((\ln \beta) \) versus \((1/T)\) obtained from DSC curves using multiple heating rates gives a straight line where the slope can be used to determine the apparent activation energy.

The apparent activation energy determined from the Flynn–Wall–Ozawa method was reported to be more reliable than that from the Friedman method. Furthermore, the Flynn–Wall–Ozawa method also was less sensitive to instrumental noise than the Friedman method due to its integral character. However, Friedman method may offer a better visual separation of more reaction steps as well as information concerning the existence of an autocatalytically activated process [11].

### 3.3 Experimental

#### 3.3.1 Materials

The epoxy (EPON 828) was first mixed with the curing agent (EPIKURE W) at a
ratio of 24 to 100 by weight as control samples. The basic structures of epoxy and the curing agent used in the experiments were shown in Fig.3.2. The prepared re-GNFs solutions (LNR) were further mixed with one control sample to form the re-GNFs modified epoxy samples with 0.3 wt% fiber loadings. To uniformly disperse the re-GNFs in the samples, a glass rod was used to stir the mixture at room temperature until the samples turned into black color and then degassed in a vacuum oven to remove the air include during the mixing process and finally followed by sonication for 1 h. Ice cube was added every 10 min to absorb the heat generated during the sonication process.

Fig.3.2 Basic structures of epoxy (EPON 828) and the curing agent (EPIKURE W)

3.3.2 DSC measurements

About 8-10mg of the re-GNFs modified epoxy and pure epoxy samples were weighed and loaded onto the aluminum crucibles. The lid was sealed onto the crucible and then the sample was immediately placed in the DSC furnace. For every curing experiment, fresh mixture of curing agent and epoxy samples with the re-GNFs solutions were used. To establish equilibrium, a settling time of about 30s was set. All DSC curing experiments were taken with a dry nitrogen gas flow of 80 mL/min.
Thermal analysis was performed using a TA instruments (TA 2910 Differential Scanning Calorimeter). Dynamic scans of the sample were made at the rates of 2, 5, 8, and 10 °C/min, respectively, over a temperature ranging from 25 °C to 320 ºC. Runs were taken using an empty cell as a reference. DSC analysis for each sample was repeated three times. The corresponding reaction was supposed to end when the rate curve leveled off to the baseline. The heat flow data, which is a function of temperature and time, were achieved by integrating the area under the peak of the exotherm. These data were further processed to extract the fractional conversion and the rate of reaction.

3.4 Results and discussion

The dynamic thermograms obtained on pure epoxy system and the re-GNFs modified epoxy systems were reported in Fig.3.3. It was shown that a main exothermic peak of the curing reaction for pure epoxy and the re-GNFs modified epoxy systems appeared, and hence the total area under the thermograms peak based on the baseline of the curves was approximately the total heat of the reaction during the whole cure reaction.
Fig. 3.3 Non-isothermal DSC curves from curing of the re-GNFs modified epoxy and pure epoxy resins (a) pure epoxy; (b) re-GNFs modified epoxy

Table 3.1 represented the onset temperature (T<sub>i</sub>), peak temperature (T<sub>p</sub>), final cure temperature (T<sub>f</sub>), and heat of curing (ΔH) in the re-GNFs modified epoxy and
pure epoxy systems. It can be observed that the onset, peak, and final cure temperature increased with increasing heating rates for two systems because the lower heating rate favored a larger number of chemical groups to react. The results also indicated that the addition of re-GNFs retarded the cure reaction in the initial stage of cure reaction so that relatively higher temperature was needed to initiate the cure reaction compared to pure epoxy because of the steric hindrance from the re-GNFs [12]. This delayed initial cure reaction behavior was further verified as shown in Fig. 3.4. At low temperature range the steric hindrance of nanofillers interfered with the mobility of the reacting species, disrupted the reaction stoichiometry on the local scale, and resulted in decelerating the propagation reaction. In order to overcome the steric hindrance of the nanofillers and activate the initial cure reaction, more heat energy input and so higher temperature were needed at the beginning of the reaction. However, it was not the case at higher temperature range. The higher temperature prompted the mobility of the reacting species, increased the local density of the reacting species, and promoted the cure reaction. On the other hand, the high thermal conductivity of the re-GNFs further weakened the retarding effect of the steric hindrance from the addition of nanofillers [12]. Furthermore, according to the amine-epoxide polymerization reaction, the reactive hydroxyl groups on the surface of re-GNFs also participated in an opening of the epoxide rings like an amino curing agent, reacted with epoxy to form the ester bond, and facilitated the primary amine-epoxide reaction. Thus, the re-GNFs played a catalytic role in the curing reaction evolution. Higher reaction heat of curing from the re-GNFs modified epoxy samples over that of pure
epoxy also implied that the extent of cure for the re-GNFs modified epoxy samples was larger than that of pure epoxy samples.

Table 3.1 Initial curing temperature, peak temperature, final cure temperature, and heat of curing in the re-GNFs modified epoxy and pure epoxy systems

<table>
<thead>
<tr>
<th>Heating rate (°C/min)</th>
<th>2</th>
<th>5</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pure epoxy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_i) (°C)</td>
<td>67.6</td>
<td>76.6</td>
<td>84.7</td>
<td>82.1</td>
</tr>
<tr>
<td>(T_p) (°C)</td>
<td>154.1</td>
<td>177</td>
<td>191.2</td>
<td>198.1</td>
</tr>
<tr>
<td>(T_f) (°C)</td>
<td>282.9</td>
<td>295.9</td>
<td>307.5</td>
<td>317.3</td>
</tr>
<tr>
<td>(\Delta H) (J/g)</td>
<td>356.8</td>
<td>374.1</td>
<td>354</td>
<td>357.5</td>
</tr>
<tr>
<td><strong>re-GNFs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_i) (°C)</td>
<td>76.9</td>
<td>78.5</td>
<td>93</td>
<td>93.3</td>
</tr>
<tr>
<td>(T_p) (°C)</td>
<td>156.2</td>
<td>177.6</td>
<td>191.9</td>
<td>199.1</td>
</tr>
<tr>
<td>(T_f) (°C)</td>
<td>284.7</td>
<td>297.3</td>
<td>311.7</td>
<td>329.2</td>
</tr>
<tr>
<td>(\Delta H) (J/g)</td>
<td>391.2</td>
<td>407.7</td>
<td>369.6</td>
<td>394.4</td>
</tr>
</tbody>
</table>
Fig. 3.4 The fractional extent of conversion with temperature of re-GNFs modified epoxy and pure epoxy systems (a) 2 °C/min, (b) 5 °C/min
The catalytic effects of the re-GNFs on the curing reaction rate can be clearly observed in Fig. 3.5. At a given degree of conversion, the re-GNFs modified epoxy system had faster reaction rate and less time needed to reach the final cure reaction over pure epoxy system. It was found that the re-GNFs modified epoxy system was slightly faster in reaching the exothermic peak than the pure epoxy system. This observation was consistent with the previous analysis. This behavior became more apparent in Fig. 3.6. At the early stage of the cure reaction the reaction rate of conversion was slow for both systems. With the cure reaction progressed, the maximum rate of conversion appeared at about $\alpha =0.5$ for the re-GNFs modified epoxy system and at about $\alpha =0.42$ for the pure epoxy system. The curing acceleration from re-GNFs can bring positive effect on the processing of composites since it needs shorter time for curing completion and save more energy. This observation was consistent with the results of Kenny et al [12]. However, the studies by Tao et al. found that nanofillers without surface treatment initiated curing at a lower temperature relative to the neat resin, while the overall degree of cure was lower [13]. Therefore, we can conclude that during epoxy cure, the pure resin begins to cure first, as shown by its lower temperature and shorter onset time in DSC experiments. As the reaction proceeded, the enthalpy of reaction increased and larger extent of cure was finally achieved for the re-GNFs modified epoxy system.
Fig. 3.5 The curing reaction rates of the re-GNFs modified epoxy and pure epoxy systems at 2 °C/min

Fig. 3.6 The curing reaction rates vs. the degree of conversion of the re-GNFs modified epoxy and pure epoxy systems at 2 °C/min
It has been known that the reaction activation energy $E_a$ represents the potential barrier and the evolution mechanism of the cure reaction. It is generally believed that the reaction activation energy of epoxy resins is not constant during the cure reaction but the function of the degree of conversion [14]. As described above, the Friedman method and the Flynn-Wall-Ozawa method can be used. The main advantage of two methods is that the reaction activation energy can be directly derived without the assumption of the kinetic model of the reaction mechanism. Therefore, the effects of the re-GNFs on kinetic parameters of curing reaction of the epoxy were further studied according to the Flynn–Wall–Ozawa method based on its advantages.

Figures 3.7 (a) and (b) showed the plots of $\ln(\frac{d\alpha}{dt})$ versus $\left(\frac{1}{T}\right)$ for the pure epoxy and the re-GNFs modified epoxy systems, respectively. To obtain the change of reaction activation energy during the cure reaction, a set of $\alpha$ was chosen from the full range of experimental data at the multiple heating rates, i.e. $\alpha = 0.10, 0.2, \ldots, 0.90, 1.0$. Based on the Flynn-Wall-Ozawa method through linear fitting of $\ln(\beta)$ versus $1/T$, the values of $E_a$ were obtained for a particular $\alpha$. 
Fig. 3.7 FWO plots at various degrees of conversion for epoxy systems. (a) pure epoxy system; (b) the re-GNFs modified epoxy systems

Figure 3.8 presented the plot of $E\alpha$ versus $\alpha$ for the pure epoxy and the re-GNFs modified epoxy, respectively. From the figures, it can be observed that the values of
$E\alpha$ were apparently different for different $\alpha$ and exhibited a significant change during the cure reaction for two epoxy systems. In the early stages of the cure reaction the higher activation was needed to initiate the chemical reactions for the re-GNFs modified epoxy system over pure epoxy, but in the later stages the lower values of the activation energy were obtained in the re-GNFs modified epoxy system. The retarding and catalytic effects of the re-GNFs on the cure reaction of epoxy systems in the different stages contributed to the competition of the steric hindrance and the participation of the reactive functional group in the reaction from the re-GNFs. The obtained values of the activation energy during the cure reaction reflected this behavior of the re-GNFs.

![Graph showing the dependence of activation energy ($E\alpha$) on the degree of conversion ($\alpha$).](image)

Fig. 3.8 Dependence of activation energy ($E\alpha$) on the degree of conversion ($\alpha$)

Polynomial regression methods were taken to fit curves to the data of the activation energy. From the shape of the curves as shown in Fig. 3.8, a cubic
polynomial could be sufficient to fit for both systems. The fitted equations for both epoxy systems were given as:

For pure epoxy system:

\[ E(\alpha) = 52.7096 + 58.52144\alpha - 131.68651\alpha^2 + 92.89562\alpha^3, \alpha \in (0,1) \]  
(3.16)

Adjusted R\(^2\)=0.98907

For the re-GNF modified epoxy system:

\[ E(\alpha) = 57.945 + 36.4596\alpha - 87.43182\alpha^2 + 63.035556\alpha^3, \alpha \in (0,1) \]  
(3.17)

Adjusted R\(^2\)=0.99909

Apparently there existed two values of E\(_\alpha\) for dE\(_\alpha\)/d\(\alpha\) = 0. At the beginning of cure reaction, the value of E\(_\alpha\) for the re-GNFs modified epoxy system was larger than that of pure epoxy; with cure reaction proceeding, the tendency changed. Therefore, although at the starting stages retarding effect on cure reaction, at the last stages of cure reaction the re-GNFs offered a catalytic influence on the cure reaction of epoxy.

As comparison, we checked whether the obtained kinetic parameters from the Flynn-Wall-Ozawa method could consist with constant activation energy (E). Constant activation energy method depends on only a specific temperature of the curing DSC curves, i.e. peak temperature, and uses one heating rate at a time, not a set of temperatures and multiple heating rates. The value of E can be determined from the slope of the plot of –ln(\(\beta\)) vs. 1/T\(_p\) as shown in Fig. 3.9. The obtained values of the activation energy were 58.28 and 61.57 kJ/mol for pure epoxy and the re-GNFs modified epoxy systems, respectively. These values of the activation energy were located in the range of the activation energy from the Flynn-Wall-Ozawa method.
From the above analysis, it can be concluded that the Flynn-Wall-Ozawa method fitted well with the experimental results and the variable E method was more effective in studying the cure kinetics of epoxy resins compared to constant E method.

Fig. 3.9 Linear plot of $-\ln(\beta)$ vs. $1/T_p$ based on constant activation energy method (a) pure epoxy; (b) re-GNF modified epoxy
3.5 Conclusions

The effect of the re-GNFs on the cure behavior of the epoxy resin was studied using non-isothermal differential scanning calorimetry. The results of kinetic analysis indicated that compared to pure epoxy; the re-GNFs modified epoxy system exhibited an evident catalytic action at the later stages, although the re-GNFs slightly retarded the cure reaction of epoxy resin at the early stages. Therefore, the catalytic curing behavior of the epoxy resin resulting from the addition of re-GNFs can save cure time/energy for a cure cycle, which is of practical importance.

Reference


CHAPTER 4 CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

Our research work has addressed the effects of GNFs with and without different functional groups at extremely low loading levels (< 1 wt %) of wetting behaviors and flowability of epoxy matrix. Thorough examination of curing evolution of the re-GNFs modified epoxy matrix has been provided.

First, the study results showed that GNFs with different functional groups led to very different effects on surface tension, advancing contact angle, and viscosity of epoxy resin. In particular, our previously developed "liquid nano-reinforcement" with a kind of re-GNFs not only effectively improved wettability for the epoxy, but also contributed to extraordinary flowability for the epoxy matrix through reduced viscosity. For example, 0.3 wt% re-GNFs epoxy samples, caused an approximately 25% drop over the pure epoxy sample. This re-GNFs modified epoxy also exhibited improved spreading and wetting behaviors on the rough fabric surfaces. In the experimental observations no trapped air pockets were found in the re-GNFs modified epoxy samples. The formed quasi-continuous contact line of the re-GNFs modified epoxy samples on the rough fabric surfaces predicted good spreading and wetting characteristics over pure epoxy.

It is the first time to obtain images of wetting behaviors for epoxy resin on the fabric surfaces in labs. The experimental observation showed that the basic models developed by Wenzel and Cassier-Baxter may be used to explain the observed difference in wetting behaviors between pure epoxy and re-GNFs modified epoxy
resins on the horizontal fabric surfaces. The experiments of the two systems on the tilted fabric surfaces further verified the difference of wetting behaviors observed on the horizontal fabric surfaces. Furthermore, a dry-wet contact model was developed to characterize the significantly different behaviors of dynamic wetting processes between pure epoxy and re-GNFs modified epoxy resins on the horizontal and tilted fabric surfaces, which cannot be represented by existing reported models. The re-GNFs modified epoxy resin has been shown to have unique wetting and flow behavior, which is significant for application in FRP manufacturing as the matrix material.

Secondly, to characterize the effects of re-GNFs on the curing cure kinetics of epoxy resin, the dynamic mode of DSC was used in the investigation. The results from the experimental observation and kinetic analysis indicated that although in the initial stages of cure reaction, the addition of re-GNFs slightly retarded the cure reaction because of the steric hindrance from the re-GNFs, the re-GNFs provided a catalytic action for the cure reaction of epoxy resin by participation in an opening of the epoxide rings like an amino curing agent and facilitating the primary amine-epoxide reaction. Therefore, the re-GNFs played a catalytic role in the curing reaction evolution at high temperature.

The experiments confirmed that the re-GNFs epoxy system can be used as an effective matrix material for manufacturing FRP composites. The improved wetting behavior, lower viscosity, and larger extent of cure reaction of the re-GNFs epoxy matrix can reduce the energy consumption during the manufacturing and may enable
low-energy resin infusion processing of high quality and high performance FRP composites. Therefore, this nano-modified epoxy matrix is especially appropriate for resin infusion processing and offer potential to produce high performance FRP composites.

4.2 Future work

This research mainly addressed the effects of GNF with different functional groups on wetting behaviors of epoxy resins. Extensive study of adhesion properties related to the wetting behaviors of the GNFs with different functional groups should be performed. This is because adhesion properties between matrix and fibers are highly related to the wettability of the resin system, and they will be critical for composite structures made from the nano-modified composites. In addition, we expect that the composite materials with the nano-modified epoxy matrix will have advanced performance and excellent processability, in particular for resin infusion technology. Therefore, the studies of composite materials should be carried out based on the interfacial adhesion work.